“Synthesis, Characterizations and Chemiresistive properties of the nanomaterials”

Synopsis in candidature for the award of

Doctor of Philosophy in Physics

Submitted by

Patale Gitanjali Ambadas

Under the guidance of

Dr. Santosh S. Jadhav

Dnyanopasak Shikshan Prasarak Mandal’s,

Arts, commerce and science college, Jintur (MS)-431509.

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Swami Ramanand Teerth Marathwada University,

Nanded (MS) – 431 606

Introduction

Chemiresistor is a material that changes its electrical resistance in response to changes in the nearby chemical environment [1]. Chemiresistors are a class of chemical sensors that rely on the direct chemical interaction between the sensing material and the analyte [2]. Chemical/gas sensor is the device used to detect the hazardous and toxic gases present in environment and expelled by the chemical industries and automobile fuel combustion. The rapid industrialization of our society has made it necessary for measurement technologies for monitoring of various gasses, and fumes to grow in parallel. At present, detection of toxic gases became a point of necessity to maintain the environmental balance [3]. The developments of miniature and portable gas sensor that are able to detect these gases in real time with good sensing performance will significantly impact our daily life. In the last few years there has been an explosion in the number of published papers dealing with nanomaterials for gas sensor application. Gas sensor is the device that is of supreme importance [4]. There is a need for simple, sensitive and stable electronic sensors suited for trace detection in a wide spectrum of application ranging from lab-on-chip and in vivo biosensors to environmental monitoring and warfare agent detection, as opposed to the often employed expensive, bulky and complicated instrumental method. Inexpensive and low-power devices are fuelling the exponential growth of research in this area. Researchers are trying to fabricate nanomaterials that would work as better gas sensor with fast response, long-term stability, high sensitivity, and greater selectivity. There is an important point to be concerned to control and monitor these harmful species, considering a huge risk of damage to assets and human beings if a leak occurs [5]. There are certain gases which are toxic to human and environmental lives as they cause big explosion. Accordingly, there is a need of gas sensor with the intention of continuous and effective detection of these gases to evade predominantly the above said dangers.

Literature review

There are many reports available on the gas sensing properties of the various nanomaterials against various gases. The sensitivity of the various nanomaterials like oxides/sulphides has been widely studied against volatile compounds (NH_3, C_3H_6O, CH_3OH, C_2H_5OH, etc) as well as commercial gases like NO_2, H_2S, CO, LPG, etc. Recently, Waghmare *et al.* prepared upright standing nanoplates of Pristine and palladium-doped perovskite bismuth ferrites (BFO and

Pd-$BiFeO_3$) using sol-gel auto-combustion method and studied their gas sensing properties against NO_2. With the 93% sensitivity and response/recovery time of 90/110 s, the Pd-$BiFeO_3$ shows excellent performance against NO_2 at 100 ppm concentration and 150 °C. The Pd-$BiFeO_3$ shows excellent stability up to 20 days [6]. Raut *et al.* prepred cobalt ferrite ($CoFe_2O_4$) nanoparticles using the similar sol-gel method. With the 70% response at 100 ppm the prepared material shows good performance against ammonia. The response/recovery time was 115/145 s and materials showed excellent stability after 15 days [7]. Mangu *et al.* fabricated an ammonia gas sensor based on chemically reduced graphene oxide with pyrrole vapor, Py-rGO. The response of the sensor was examined at various ammonia concentrations ranging from 5 ppb to 100 ppm, and it was shown that the sensor exhibited about 4.2 % increase in the normalized resistance upon exposure to 5 ppb of the target gas, and about 22 % increase upon exposure to 100 ppm [8]. Huang *et al.* studied an ammonia gas sensor based on reduced graphene oxide (RGO)-polyaniline (PANI) hybrids, and showed that while the unmodified RGO based sensor exhibited about 5.2% change in the normalized resistance when exposed to 50 ppm of ammonia. When used for the same ammonia concentration, the hybrid material exhibited an improved response of 59.2 % [9]. Abdelhalim *et al.* examined the response of CNT-based gas sensor functionalized with Au, toward different ammonia concentrations, varying from 10 -100 ppm. They found that upon exposure to 100 ppm of the target gas, the sensor reached normalized response of 92 % [10.]

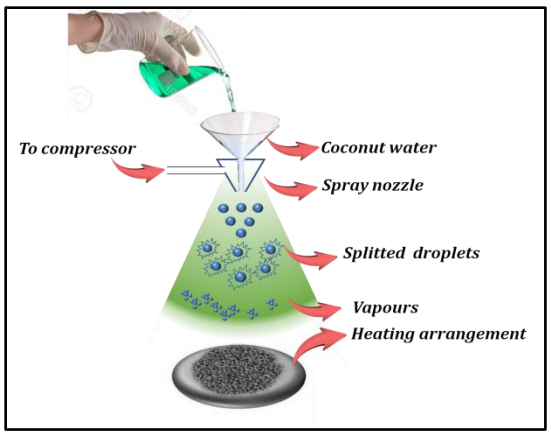
Methodology

a) Material synthesis

The required nanomaterials will be prepared using various synthesis methods like:

i) Spray pyrolysis

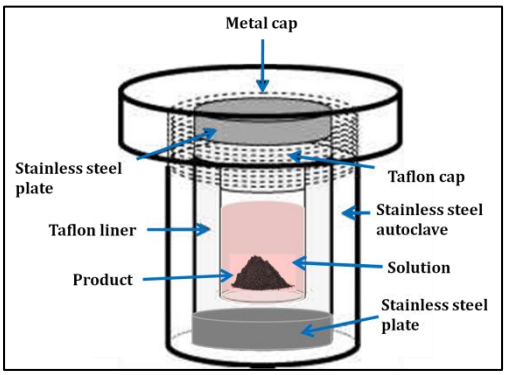
Spray pyrolysis is a technique which is frequently used to prepare dense and porous oxide films, ceramic coatings, and powders. Unlike many other film deposition techniques, spray pyrolysis offers an extremely simple and cost-effective method. This method does not require high-quality substrates or chemicals and is used for the deposition of dense films, porous films, and for powder production. Even multilayered films can be easily prepared using this versatile technique.



Scheme I: Spray pyrolysis synthesis.

ii) Hydrothermal synthesis

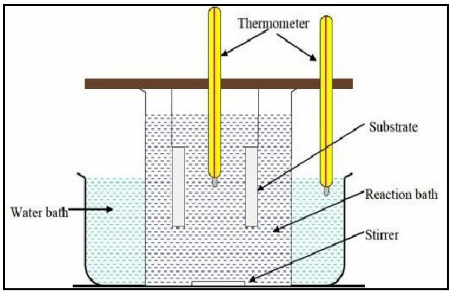
Hydrothermal synthesis method is one of the soft chemical methods used for producing nanostructures of oxides and hydroxides at the modest temperature i. e. <200°C in the sealed ceramic container wherein reagents are usually poured. The principle of this method is based on the strained hydrolysis of the reactants. Generally, water is used as a solvent in which metal salts or alkoxides can be used as a source while metal hydroxides are used as a mineralizer.



Scheme II: Hydrothermal synthesis.

iii) *Chemical bath deposition (CBD)*

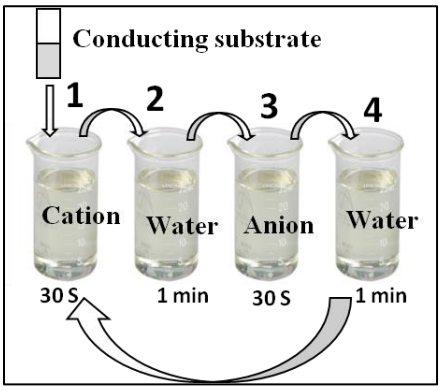
CBD is the synthesis method used to preparation of and nanomaterials and thin films. The preparation of nanomaterials or thin films occurs in two steps i. e. nucleation and particle growth which is further based on the formation of the solid phase form the mother solution. In this method, the substrate is deep in the solution of the precursors. This method depends upon various parameters like temperature, molarity and pH of the solution.



Scheme III: Chemical bath deposition.

iv) *Successive ionic layer adsorption and reaction (SILAR)*

SILAR method is economically feasible for large area deposition by which wastage of chemicals can be avoided. For the deposition of material thin film, a well-cleaned substrate immersed in the cationic precursor solution, causing cations to be adsorbed on the surface of the substrate. This substrate was immersed in sufficient amount of double distilled water to prevent homogenous precipitation. The substrate was then immersed in the anionic precursor solution. Anions reacted with the adsorbed cations on the glass substrate. The substrate was then immersed in double-distilled water.



Scheme IV: *Successive ionic layer adsorption and reaction synthesis*.

Along with these methods other methods will be adopted if necessary.

Gas sensing measurements

A schematic illustration of the sensor unit with a gas sensing experimental setup is shown in Figure 1.

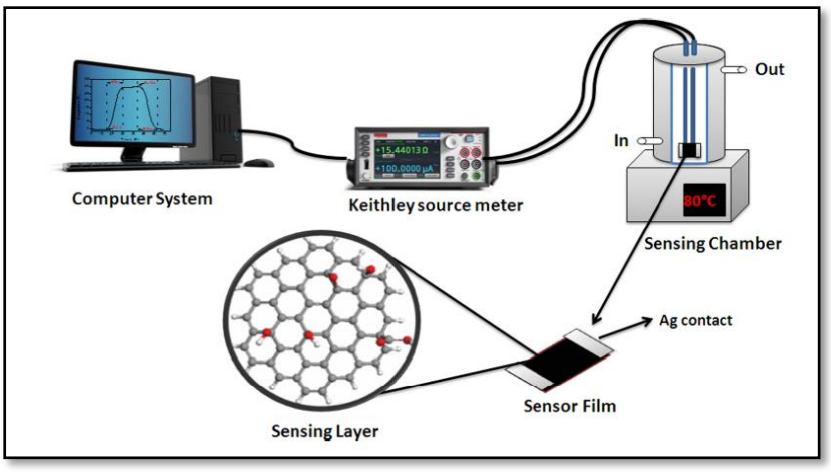


Figure 1: A schematic illustration of the sensor unit with a gas sensing experimental setup.

The gas sensor unit consists of a stainless-steel cylindrical chamber with 250 mL volume capacity. The cylindrical chamber consists of heater with PID controller to set the desired temperature. A voltage stabilizer will be used to provide constant voltage to avoid the fluctuations in the temperature. The change in resistance of the sensor, due to the presence of target gas, can be recorded by using Computer assisted 6- digit Keithley 6514 System electrometer. Keithley electrometer was coupled to the computer *via* RS232 interface to record the change in resistance with respect to time. For gas sensor measurements, the thin film of the prepared nanomaterials will be used. For electrical contacts silver paste, on the sensor film, will be preferred.

The gas response will be calculated from the following relation;

$$\boldsymbol{S}\% = \frac{\boldsymbol{R_a - R_g}}{\boldsymbol{R_a}} \times \mathbf{100} \tag{1}$$

where, R_a is the stabilized resistance of the sensor material in presence of air, R_g is the stabilized resistance in presence of the target gas. The desired concentration of target gas was obtained by the static liquid gas distribution method, which was calculated by the following formula.

$$\mathbf{C\ ppm} = \frac{\mathbf{22.4\rho TV'}}{\mathbf{273MV}} \times \mathbf{1000} \tag{2}$$

where, C (ppm) is the desired target gas concentration; ρ is (g/mL) the density of the liquid; 'V' is the volume target gas (μL), T is testing temperature (K), M is the molecular weight of target gas (g mol^{-1}), and V is the volume of testing chamber (L).

Objectives

This thesis aims at achieving the following objectives,

- To prepare the various nanomaterials using suitable synthesis method.
- To study the structural and morphological properties of the prepared nanomaterials will be studied using various characterization techniques like X-ray Powder Diffraction (XRD), FE-SEM (Field Emission Scanning Electron Microscopes), High-Resolution Transmission Electron Microscopy (HR-TEM), and energy dispersive X-ray analysis (EDS), etc.
- To measure the Chemiresistive properties of these nanomaterials for various gases.
- To study the effect of the concentration on the gas sensing properties of the prepared nanomaterials.

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